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LOGISTIC FUEL PROCESSOR DEVELOPMENT

Reza Salavani
Aly H. Shaaban
Timothy Campbell
Mikel Sawyer
Richard Trotta
Russ Hallett

PERFORMING ORGANIZATION:

AIR FORCE RESEARCH LABORATORY
MATERIALS & MANUFACTURING DIRECTORATE
AIRBASE TECHNOLOGIES DIVISION
139 BARNES DRIVE, STE 2
TYNDALL AFB FL 32403-5323

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-S-   -S-
REZA SALAVANI, DR II, DAF   RICHARD N. VICKERS, DR-IV, DAF
Program Manager   Chief, Deployed Base Systems Branch

-S-
JIMMY L. POLLARD, Colonel, USAF
Chief, Airbase Technologies Division

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Aly Shaaban, Tim Campbell, Mikel Sawyer, Richard Trotta, and Russ Hallett

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AFRL/MLQD
139 Barnes Drive, Suite 2
Tyndall AFB FL 32403-5323

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Mr. Reza Salavani
AFRL/MLQD
139 Barnes Drive, Suite 2
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The Air Base Technologies Division of the Air Force Research Laboratory has developed a logistic fuel processor that removes the sulfur content of the fuel and in the process converts logistic fuel to light gases then steam reform the light gases into hydrogen rich stream. This report documents the efforts in developing a fuel processor capable of providing hydrogen to a 3kW fuel cell stack. The technical challenges in the development of this technology included development of a fractionation device to reduce the size of sulfur scrubber beds, a cracking process with high conversion efficiency, and the reduction of cocking potential of fuel reforming.

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Executive Summary

The rapid evolution of fuel cell technology as a replacement for conventional electric power generators has provided a gateway to future power systems using hydrogen as the primary fuel. With their high cycle efficiencies, in excess of 60%, and simplicity of operation, fuel cells afford the user high reliability and efficient use of primary energy in the form of hydrogen. The major drawback to militarize the use of fuel cells has been the inability to effectively use battlefield fuels as the primary energy source. The ability to reform battlefield fuels to hydrogen would allow use of fuel cells in place of conventional generators. This would result in power generation systems with higher efficiency, lower emissions, lower IR signature, and lower noise levels.

The Air Base Technologies Division of the Air Force Research Laboratory has developed a logistic fuel processor that removes the sulfur content of the fuel and in the process converts logistic fuel to light gases then steam reform the light gases into hydrogen rich stream. This report documents the efforts in developing a fuel processor capable of providing hydrogen to a 3kW fuel cell stack. The technical challenges in the development of this technology include development of a fractionation device to reduce the size of sulfur scrubber beds, a cracking process with high conversion efficiency, and the reduction of cocking potential of fuel reforming.

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NOMENCLATURE

FW	chemical Formula Weight
LFP	Logistic Fuel Processor
MEP	Mobile Electric Power
NBP	Normal Boiling Point (at one atmosphere)
NVR	Non-Volatile Residue
PEMFC	Proton Exchange Membrane Fuel Cell
SOFC	Solid Oxide Fuel Cell
S/C	Steam to Carbon ratio

1. INTRODUCTION

Increasing destabilization within many regions of the world poses an imminent threat to vital U.S. interests, requiring rapid response and "light, lean and lethal" force deployments. As illustrated by recent events, the United States must be increasingly prepared to rapidly deploy and indefinitely sustain intervention forces. Coupled with overseas base reductions however, DoD must now rely almost exclusively on mobile, air deployable infrastructure elements to stage and support U.S. air and land operations in many remote locations globally.

Mobile Electric Power (MEP) is one of five essential infrastructure elements in Tri-service deployments. The Army Force Providers and the Air Force Bare Bases are examples of Tri-service extensive use of MEP generators. MEP accounts for 8 C-141 sorties per 1100-man deployment and up to 4,000 gallons per day of fuel sustainment, placing a severe burden on an already stressed air fleet.

The rapid evolution of fuel cell technology as a replacement for conventional electric power generators has provided a gateway to future power systems using hydrogen as the primary fuel. With their high cycle efficiencies, in excess of 60%, and simplicity of operation, fuel cells afford the user high reliability and efficient use of primary energy in the form of hydrogen. The major drawback to militarize the use of fuel cells has been the inability to effectively use battlefield fuels as the primary energy source. The ability to reform battlefield fuels to hydrogen would allow use of fuel cells in place of conventional generators. This would result in power generation systems with higher efficiency, lower emissions, lower IR signature, and lower noise levels.

The military has standardized its battlefield energy on so-called 'logistic fuels'. Conversion of these fuels for use in fuel cells would provide the military the ability to use this new and important technology as well as provide further impetus to fuel cell development. The fuel cell generator system will provide efficient, reliable, and environmentally safe power to bare base and Air Expeditionary Force (AEF) operations.

Fuel cells systems designed for use in the commercial sector only use clean and easy hydrogen extractable fuels such as natural gas. The Daimler-Benz vehicle, NECAR 3, powered by a fuel cells system, uses steam reforming to convert methanol into hydrogen. Logistic fuel on the other hand is not a commercially used fuel, harder to convert, and its sulfur content will poison fuel cells. Therefore, developing a logistic fuel processor is a DOD unique need. Recently developed diesel fuel reforming technologies by DARPA have large footprint and long response time characteristics, which makes them unsuitable for integration with deployable fuel cells generators. The Army and the Air Force unique need to miniaturize fuel processor require the development of a new reforming technology.

The Deployed Base Systems Branch of the Air Force Research Laboratory (AFRL/MLQD) has therefore developed a logistic fuel processor (LFP) technology suitable for mobility operations. The required characteristics of the fuel processor include small footprint, high reforming efficiency, and high hydrogen purity. It is the aim of AFRL/MLQD to combine

its LFP technology with the fuel cells technologies being developed by other DOD services and DOE to produce the next generation of MEP generator systems.

2.   OBJECTIVES

The main objective is to develop a compact logistic fuel processor with augmented heat and mass transfer, chemical reactions, and impurity removal. The major objective of this effort is to develop a 3-kW fuel processor for proof of concept.

3.   RESEARCH PROGRAM

3.1   Design Basis

In processing heavier hydrocarbons such as military logistic fuels (JP4, JP5, JP8, and JP100), kerosene, and diesel to hydrogen for fuel cell use, several issues arise. One issue is the numerous components required to process the fuel, making the processor unit bulky. Second, the high sulfur content represents a major obstacle to the use of these fuels. Third, JP-8 is known to contain up to 1.5% (v/v) Non-Volatile Residue (NVR), which could potentially foul the fuel processor. The fourth issue is the coking potential of reforming heavy hydrocarbons.

Current technologies use between 10 and 12 components to process the fuel. These components include a steam reformer reactor, high temperature and pressure steam generator, high pressure and temperature fuel evaporator, two water-gas-shift reactors each at different temperature, a carbon monoxide catalytic oxidation reactor, and a number of heat exchangers to maintain process temperatures. For distillate fuels a sulfur removal unit is added. The large number of components results in a sizeable fuel processor with a large footprint to compete with current electric generators.

Desulfurization of JP-8 requires removal of all of the classes of sulfur compounds, either by direct adsorption, or by dissociation to hydrogen sulfide (H_2S), which is subsequently removed by adsorption or other separation techniques. Direct adsorption of organo-sulfur species in a single-stage scrubber is a simple process that can be conducted at ambient temperature and pressure. Adsorbents used to desulfurize petroleum feedstocks in refinery operations include molecular sieves and activated charcoal [1].

Direct adsorption is impractical for use in a deployable fuel reformer, however, because the adsorbents have limited capacities for benzo- and dibenzothiophenes, so that large bed volumes are required, and because the adsorbent beds must be periodically regenerated with low-pressure steam, significantly diminishing overall process efficiency. Thermal dissociation, or catalytic cracking, of mercaptan and alkyl sulfide species yields H_2S and unsaturated aliphatic products directly [2].

In removing sulfur content of the fuel, current practices use a hydro-treatment process. Different hydro-treatment processes were developed with emphasis on hydrogen consumption rate and purity level. Phillips Petroleum Company developed SZorb process claiming low hydrogen consumption for both gasoline and diesel that requires less pure hydrogen stream than other processes. Downsizing these technologies to fit into a fuel processor for hydrogen

generation is not practical and the mere requirement of hydrogen feed makes this approach not suitable for reforming process for fuel cell use.

Another approach is the cracking process where sulfur compounds are converted to hydrogen sulfide followed by a reaction in zinc oxide (*ZnO*) packed bed that converts hydrogen sulfide to zinc sulfide and water. In this process zeolites are used as cracking catalyst. It is prone to coking and the cracking reactor requires constant regeneration using high temperature steam. The zinc sulfide produced in the absorption bed is a stable compound requiring periodic replacement. Because of the high sulfur content in these fuels, the sulfur absorption bed would have to be very large to accommodate a reasonable operating period, even if a regenerative cycle to absorb H_2S is developed.

Coke formation is a frequent occurrence in heavy hydrocarbon steam reforming processes. Current practices use high steam to carbon ration to discourage coking or use high temperature steam to regenerate steam-reforming reactor.

Development emphasis has been on a fuel processor concept that reduces the number of components with a separate unit to recover water from fuel cell exhaust, while removing sulfur from the fuel feed and eliminating coking potential.

3.2   Fuel Processor Components

A fuel processor concept that consists of three groups, Figure 1, has been developed. The first is a sulfur removal group that consists of a fractionator, cracking reactor, and sulfur scrubber beds. The second is a steam reforming group that consists of a steam generator and a steam reformer with or without embedded hydrogen membrane. The third group is a recovery unit to extract water from fuel cell exhaust. The addition of the embedded hydrogen membrane results in the elimination of water-gas-shift reactors, CO oxidizer units, and a number of heat exchangers, increase the reforming process efficiency, while delivering pure hydrogen to PEM fuel cells. When a solid oxide fuel cell is used, pure hydrogen is not required; hence, the hydrogen membrane is not needed.

3.2.1   Sulfur Removal Group

The sulfur removal group includes a fuel partial evaporator (fractionator), a cracking reactor, heat exchanger, gas-liquid separator, and two sulfur absorption beds.

The developed concept is based on the sulfur distribution in each of these fuels and the portion of the fuel feed needed to provide the thermal energy required by the endothermic processes. Using heat and mass balance calculations with a surrogate fuel formula for JP-8 it was estimated that 34wt% of JP-8 feed must be combusted to provide the heat necessary for vaporization and steam reforming of the remaining 66wt% at a steam/carbon ratio of 4:1 and at 1 atmosphere operating pressure. This design criterion raised the question of which portion of the fuel fractions should be used to provide the 34wt% needed for combustion. To answer this question, a study was conducted to evaluate the sulfur distribution in the fuel fractions. Diesel, JP8, gasoline, and kerosene were analyzed, however, here only JP8 results are given.

Using Boiling-Point Gas Chromatography, JP-8 samples were analyzed for both carbon and sulfur compounds, Figure 2. JP-8 is a kerosene-range distillate containing carbon compounds from C_6 to C_{18}, with about 90% of the mass from C_9 to C_{16}; the center of mass is C_{11}. JP-8 typically contains approximately 490ppm total sulfur [4]. The total sulfur specification for JP-8 is 0.30 mass percent maximum [5]. Sulfur in JP-8 is present primarily as organo-sulfur compounds, including alkyl and aromatic sulfides and mercaptans, thiophenes, benzothiophenes, and dibenzothiophenes. Table 1 lists structures and properties of some representative organo-sulfur species present in JP-8.
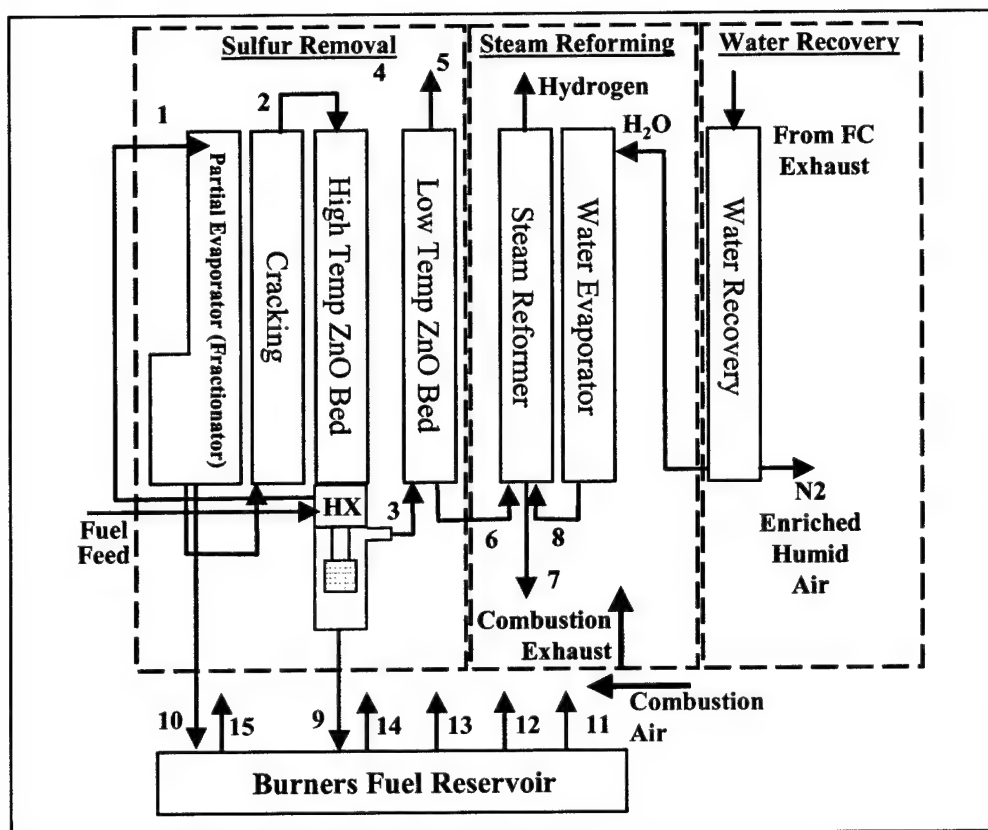
Figure 1: Components and flow streams of proposed fuel processor; The stream numbers are explained in Appendix I along with component descriptions.

The instrument used for all gas chromatographic (GC) analyses was a Hewlett-Packard 6890 equipped with Helium carrier gas (UHP zero grade, UN1046), split injection, and a 30m L by 0.32 mm ID SPB-1 SULFUR column, 4-µm (micron) film thickness (Supelco). Flame ionization detection (GC-FID) determined the mass-distribution of hydrocarbon in JP-8 samples and fractions using 0.4 µL sample volume injected at a split ratio of 50:1. The oven was programmed for 80°C initial temperature, 0 min initial hold, ramp at 8°C/min to 280°C, 10 min final hold. Injector and detector temperatures were at 280°C. Pulsed flame photometric detection (GC-PFPD) determined sulfur mass distributions [6].

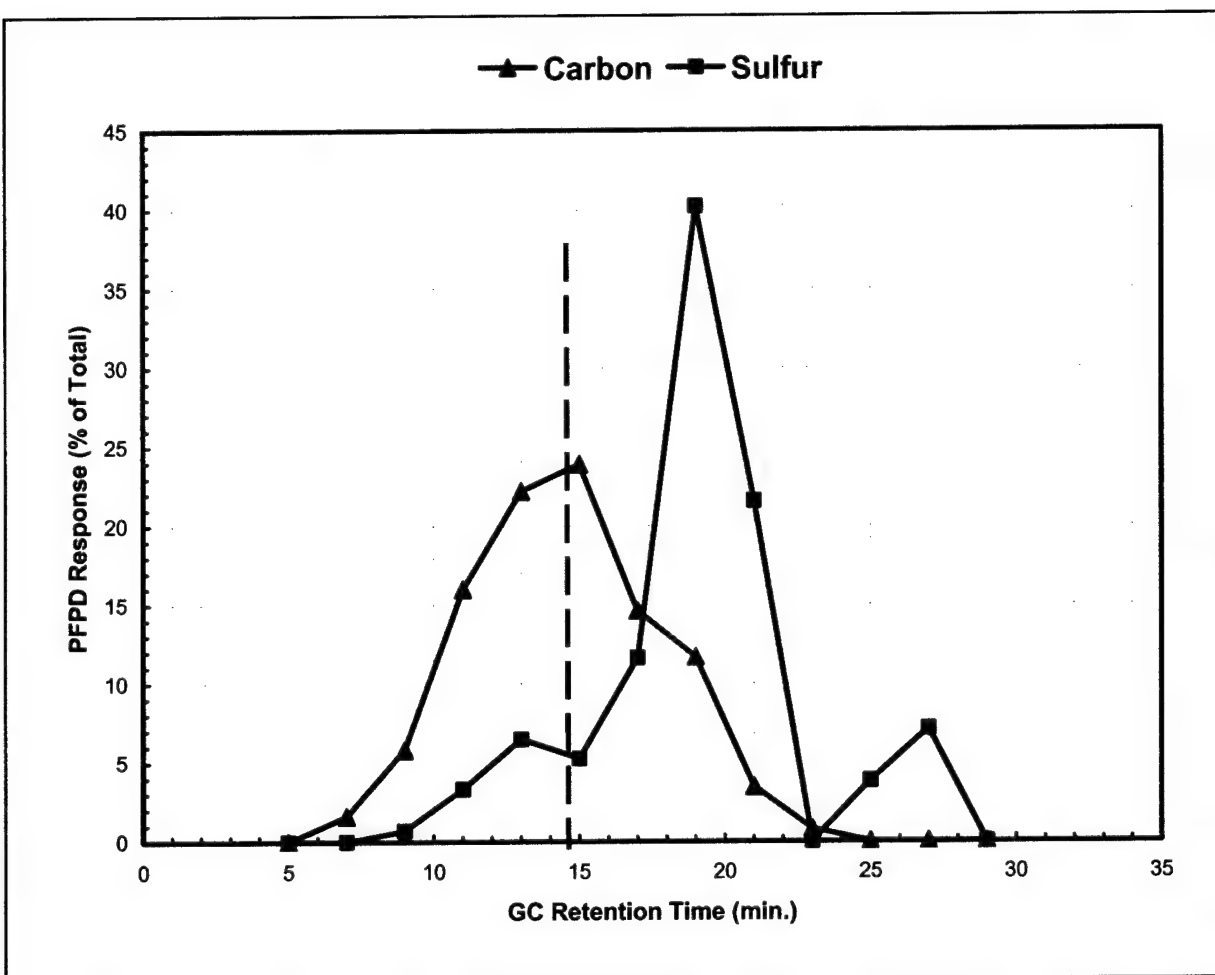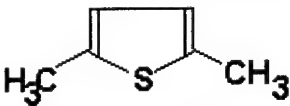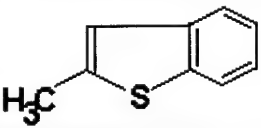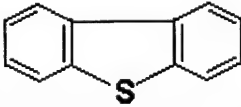Figure 2: JP-8 hydrocarbon and organo-sulfur distributions determined by GC-PFPD

The 2/3 cutoff point of the total hydrocarbon mass contains alkyl sulfides, disulfides, and substituted thiophenes. These compounds comprise about 15% of the total sulfur. Making up the remaining 85% of the total sulfur are higher boiling alkyl-substituted thiophenes, benzothiophenes, and dibenzothiophenes. The C_1, C_2, and C_3 alkyl substituted benzothiophenes elute chromatographically in the boiling range of 200 to 300°C. This corresponds to the boiling range of C_{13} through C_{18} hydrocarbons.

While all of the sulfur compounds in JP-8 have the potential to poison precious metal in fuel processor components and fuel cell stack, alkyl sulfides and thiophenes are relatively easy to remove from process streams using catalytic cracking combined with adsorbents such as ZnO.

Table 1: Classes of organo-sulfur compounds in JP-8

Class	Example	FW	NBP[9]	Decomposition

		(g/mol)	(°C)	Temp[10] (°C)
Alkyl mercaptans	1-Hexanethiol $CH_3(CH_2)_5SH$	118	152	200
Alkyl sulfides	Ethyl disulfide $C_2H_5-S-S-C_2H_5$	122	152	250
Aryl sulfides	Phenyl sulfide $(C_6H_5)_2S$	186	296	450
Thiophenes	2,5-Dimethylthiophene	112	140	475
Benzothiophenes	2-Methylbenzo[*b*]thiophene	148		>500
Dibenzothiophenes	Dibenzothiophene	184	333	>550

In Figure 2 the left side of the vertical dashed line marks two thirds of the fuel by weight, which contains only about 15 % of the total sulfur in the fuel. The approach to remove sulfur before admitting fuel to the steam reformer consists multiple steps, starting with partial evaporation of the fuel. The evaporated fraction is sent through a cracking process, followed by a sulfur absorption step (Figure 1). Approximately two thirds of the fuel is desulfurized and admitted into the steam reformer. This portion of the fuel is the light fractions in the range of C5-C15. The rest of the fuel still contains its sulfur and is used in the burners providing the thermal energy required in processing the other two thirds.

The main advantage of this approach stems from the fact that only 15% of the sulfur in the feed must be removed by subsequent cracking and absorption in order to provide zero-sulfur fuel to reformer reactor. This results in a compact design of cracking and absorption beds. The partial evaporation approach also permits management of the nonvolatile hydrocarbon species that are normally present in JP-8. JP-8 can contain up to 1.5 vol% nonvolatile residue (NVR) [5]. This NVR is composed primarily of multi-ring polyaromatic hydrocarbons such as asphaltene, which have no significant vapor pressure at temperatures as high as 400°C. JP-8 feed containing 1 vol% NVR would clog the fuel evaporator, in the conventional design, after processing 100 evaporator volumes of feed, decreasing heat transfer and reducing evaporator efficiency. Entrained liquid NVR carried over to the desulfurization reactor would coat the cracking catalyst, causing coking and deactivation. These problems are obviated by the partial evaporation approach, in which any NVR present in the feed is carried over to the burner. In the high temperature, oxidizing conditions of the burner, NVR compounds should decompose and combust.

To separate the lighter two-thirds from the heavier one-third of the fuel feed, partial evaporation is applied between 230C and 300C, depending on system pressure. More than two thirds of the fuel evaporate and sent to the cracking reactor. Meanwhile the heavy fractions stays in liquid form and is collected in the burners' fuel reservoir. These "bottoms" represent about one third of the fuel. The most refractory organo-sulfur and non-volatile hydrocarbon species should be concentrated in this high-boiling liquid. The lighter vapor fractions portion is considerably easier to desulfurize and reform than the whole fuel feed.

Cracking only the light fractions of the fuel results in two major advantages. First, much lighter hydrocarbon compounds are reformed than if fuel were fed straight to the reformer, which diminishes the probability of coking. Second, organo-sulfur compounds are converted into hydrogen sulfide, which is easily removed in absorption beds. Here the choice of catalyst plays an important role in the distribution of light fractions in the product gas. Several catalysts were investigated. These cracking catalysts included zeolites, Manganese (Mn) on alumina and others.

Before the cracked and the un-cracked fuel are separated, the mixture is cooled in a heat exchanger using the fuel and water feeds as cooling medium in a double-chamber heat exchanger. This approach has two advantages. It prevents coking due to pyrolysis in the cracking discharge tube, where the uncracked portion is kept below 450C. The other advantage is that the fuel feed is partially heated to the $300°$ C operating temperature of the partial evaporator, resulting in compact partial evaporator. The un-cracked portion is separated and sent to the burners' fuel reservoir, while the cracked gases are sent to two desulfurizer units to complete the sulfur removal process. The two desulfurizer-units are zinc oxide absorption beds. the first bed operates at 300C, the second bed is a polishing step operating at 100C. The hydrogen sulfide (H_2S) absorption capacity of a ZnO bed increases with the operating temperature of the bed [7]. At higher temperatures, faster sulfide ion transport from the surface to the interior of ZnO particles occur, so more H_2S is absorbed before breakthrough. However, the reaction $H_2S + ZnO = H_2O + ZnS$ is exothermic, so the reaction equilibrium favors the products at lower temperatures. To achieve low H_2S concentration in the ZnO bed effluent, the bed must be operated at low temperature. The use of a high-temperature "lead" ZnO bed followed by a low-temperature "lag" ZnO bed provides both good H_2S absorption capacity and low H_2S effluent concentration. When H_2S breakthrough (or "slip") is observed from the lag bed, the lead bed is discarded, the lag bed is switched to the lead position, and a fresh ZnO bed is placed in the lag position. In this way, efficient use of ZnO absorbent is combined with effective H_2S removal to protect downstream components. The result of this approach is deeply desulfurized light hydrocarbon gases are admitted to the steam reformer component.

3.2.2 Steam Reforming Group

The steam reforming group consists of a steam generator and a steam reformer. The steam generator evaporates and superheats water to provide steam for the reforming process. Superheated steam is produced at an operating temperature of 650C and pressure of 2 to 10 atmosphere. A waterside microchannel design can be used to increase the effectiveness and reduce the size of the water evaporator.

The steam reformer extracts hydrogen from the light hydrocarbon feed using steam and a catalyst. It consists of packed bed of catalyst with embedded hydrogen membrane. The hydrogen membrane allows only hydrogen to pass through, lowering hydrogen concentration at reaction sites. This configuration leads to lower operating temperature in the range of 550-650C in comparison to 1000C, and a shift in reaction thermodynamic equilibrium towards hydrogen. That thermodynamic shift results in higher conversion efficiency producing more hydrogen than conventional approach [8]. The use of hydrogen membrane eliminates the need to use the two water-gas-shift reactors and the CO burner to reduce CO concentration in the product gas.

The reforming catalyst is used to enhance the kinetics of the reaction between hydrocarbon and steam, yielding H_2, CO, and CO_2. For reforming reactors used in mobile and portable applications, a catalyst with excellent overall catalytic activity is necessary, so that maximum H_2 yield can be achieved using as small a reactor as possible. In general, steam reforming catalysts consist of a metal or metal oxide active phase dispersed on a refractory support. The metal phase can consist of nickel, cobalt, platinum, palladium, rhodium, ruthenium, iridium, or mixtures of these. The refractory support can be particles of ceramics such as alumina, ceria, silica, magnesium oxide, or calcium oxide, or can be a structured material such as an extruded porous ceramic monolith or metallic "honeycomb" material. The metal active phase can be dispersed on the support by co-precipitation, impregnation, or spray-coating techniques. Metal loading on the support can range from 2 to 20 wt%, depending on the specific surface area of the support. Steam reforming catalysts used to generate hydrogen for fuel cell applications must be formulated to have good gas shift activity, so that the CO generated by reforming reacts with excess steam to produce H_2 and CO_2, maximizing H_2 yield and minimizing CO concentration in the product stream. Reforming catalysts must also be formulated to minimize selectivity to coke formation, and to be as tolerant as possible of the presence of poisons such as sulfur, nitrogen, and metals in the hydrocarbon feed. To achieve these properties, promoters such as alkali metal oxides may be added to the active phase formula.

The steam reformer operates at 650C, while hydrogen partial pressure and fuel cell stack operating pressure determines the steam reformer operating pressure.

3.2.3 Water Recovery

The water recovery unit extracts water from the nitrogen-enriched 100% humid air leaving fuel cell stack. It is required to condense at least 68% of the water vapor in the exhaust stream for reuse in the reforming process without makeup water requirement. Two approaches can be applied. One uses condensation by cooling the exhaust stream to near ambient temperature, while the other by expanding the humid air to atmospheric pressure in a turbine. In both case the fuel cell stack will operate at high pressure and temperature and a water-air separation is applied. In the turbine application, a compressor can be installed on the turbine shaft, to provide fuel cell stack with pressurized air. The expansion energy in the turbine subsidized with a small motor enables the compressor to provide compressed air to the fuel cell stack at its operating pressure.

4. BREADBAORD PROOF OF CONCEPT

Using the concept described above, a breadboard system was designed and built. In this configuration, a palladium hydrogen membrane was used to examine its operating requirements. As shown in
Figure 3, it consisted of fuel vaporizer, fractionator, a cracking reactor, a vapor liquid separator, a steam generator, and steam reformer. All components were heated using electric heaters except the steam generator, which was heated with a JP-8 burner. The steam reformer consisted of six (6) 5/8"D x 6.5"L stainless steel inline cylinders arranged 1/4" apart, Figure 4. Each cylinder contains six (6) 3/16" diameter and 0.003" thick hydrogen membrane palladium tubes with the catalyst packed around them. The fabrication of the hydrogen membrane steam reformer unit was accomplished by REB Research and Consulting of Ferndale, Michigan.
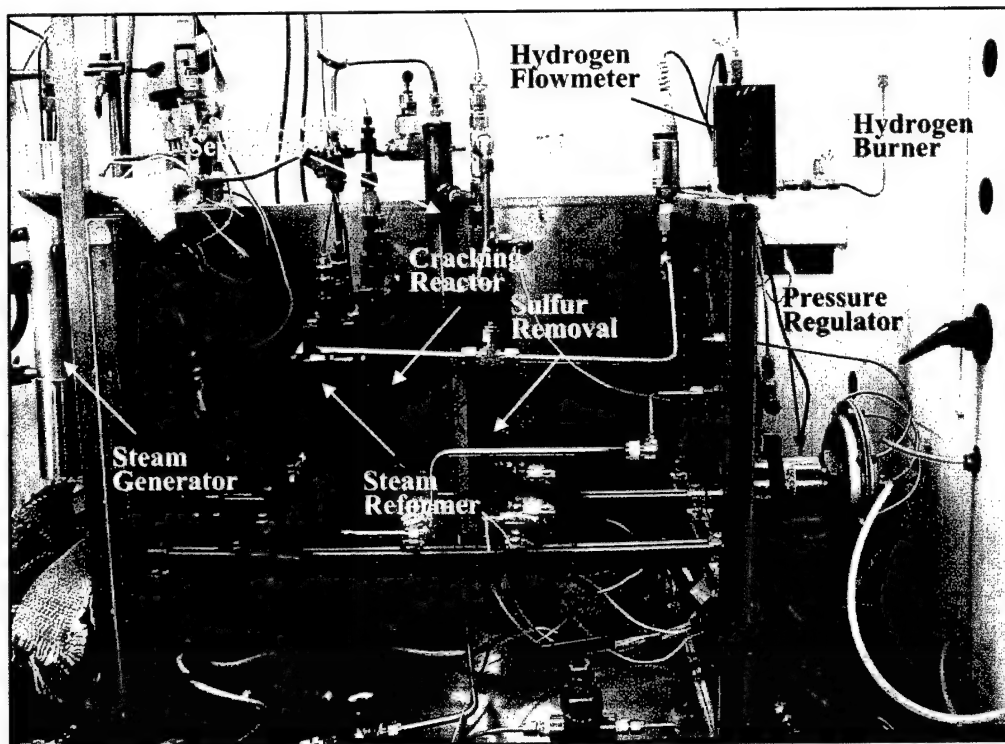

Figure 3: Breadboard System

The JP-8 processor breadboard system was examined using an experimental matrix of 9 steady-state runs (3 temperature levels X 3 pressure levels). Figure 5 shows H_2 membrane recovery (percent of H_2 produced in the reformer that was recovered as pure membrane permeate). At 553C, the membrane was nearly impermeable. Membrane performance increased with increase in temperature and pressure to a maximum of 35% recovery at 691C and 156 psig. It may be possible to achieve higher recoveries with this membrane reactor, but the system was limited by the minimum rate at which it could feed JP-8 and steam.

Markers in Figure 6 show the measured concentrations of H_2 and CH4 in the reject stream. While solid and dashed lines show equilibrium concentrations calculated for CH4 steam

reforming with gas shift at steam to carbon ratio (S/C) of five (the average ratio used in these experiments). H_2 concentration in the reject conforms to equilibrium at 553C, in agreement with the observation of poor membrane performance at this temperature. As temperature and pressure increase, H_2 concentration in the reject becomes increasingly lower than equilibrium due to H_2 removal across the membrane. CH4 concentrations were slightly lower than equilibrium for all runs.

Figure 3 shows reject CO and CO_2 concentrations. CO_2 was significantly higher than the calculated equilibrium values for all runs. It is important to note that JP-8 cracking generates hydrocarbons other than just CH4; reforming of these may explain high CO_2 concentrations, as well as the low CH4 concentrations seen in Fig 2. CO is an intermediate in reforming-gas shift system.

JP8, Steam Waste & Exhaust Gases

Pure Hydrogen

Steam Reformer With Hydrogen Palladium Membrane

A Cutout Showing Palladium Membrane Cylinders Inside Stainless Steel Shell.
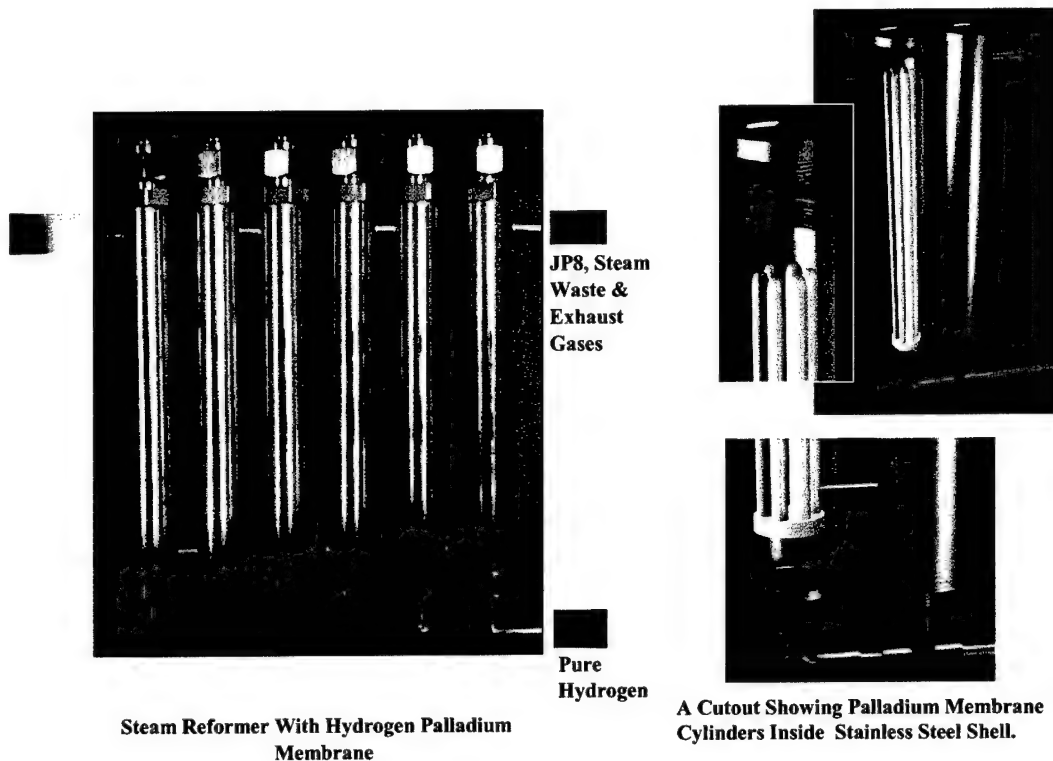
Figure 4: Steam reformer unit with hydrogen membrane, produced by REB Research and Consulting, used in Breadboard System

Figure 7 shows reject CO and CO_2 concentrations. CO_2 was significantly higher than equilibrium for all runs. It is important to note that JP-8 cracking generates hydrocarbons other than just CH4; reforming of these may explain high CO_2 concentrations, as well as the low CH4 concentrations seen in Figure 6. CO is an intermediate in reforming-gas shift system.
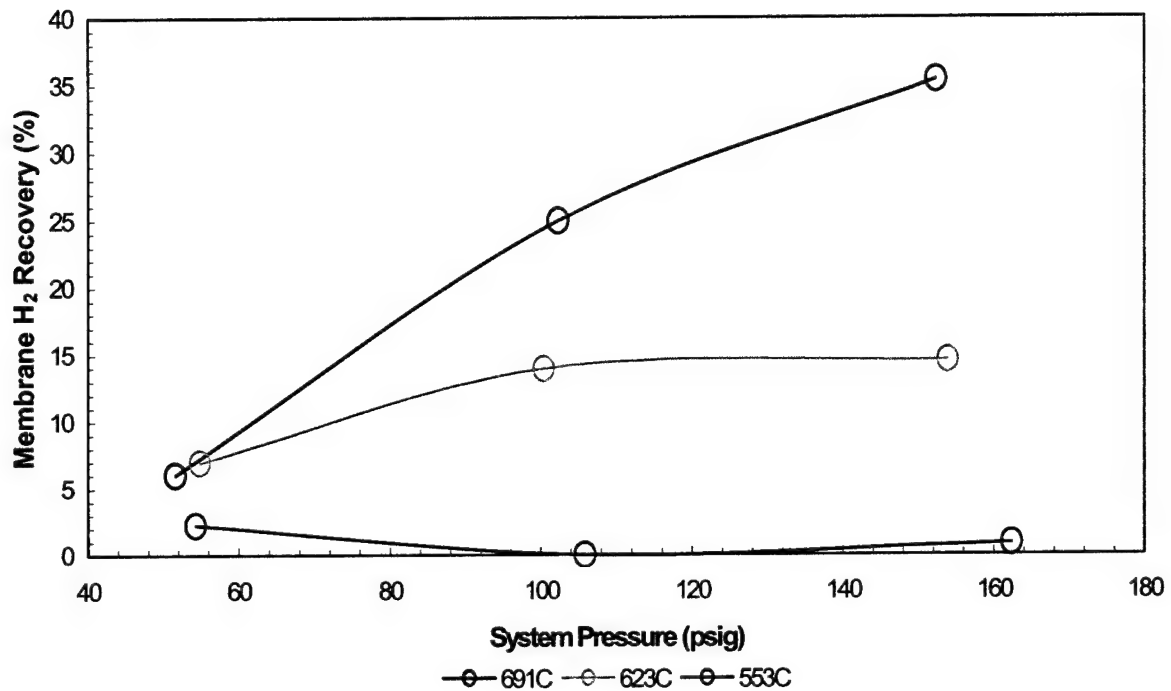
Figure 5: JP-8 Breadboard Reformer System – Percent of hydrogen recovered by purification membrane. Steady state conditions with S/C = 5
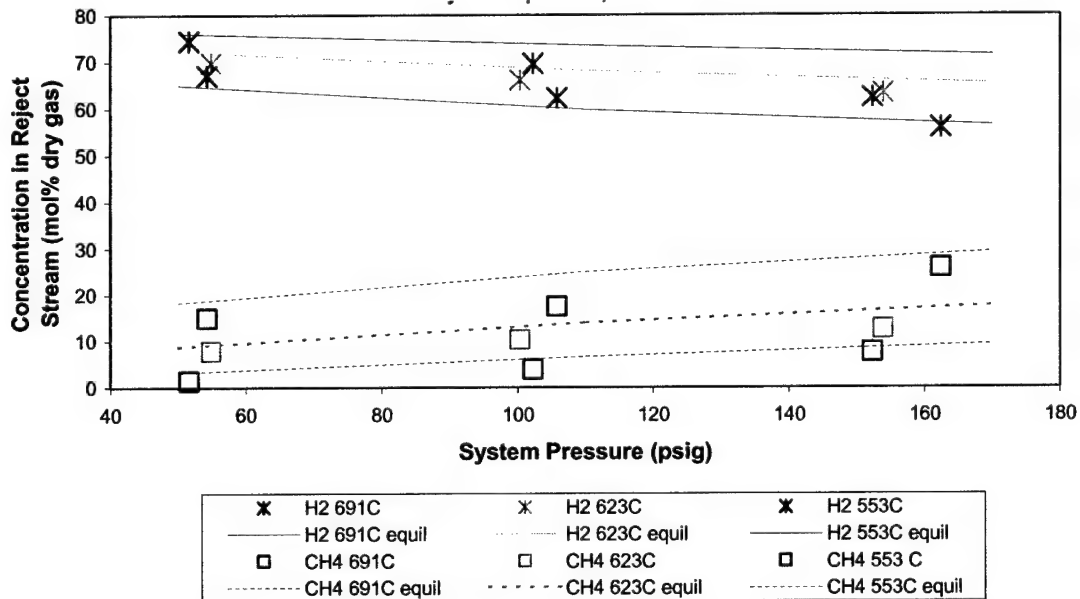

Figure 6: JP-8 Breadboard Reformer System -- Concentration of primary components in reject stream at steady state conditions with S/C = 5
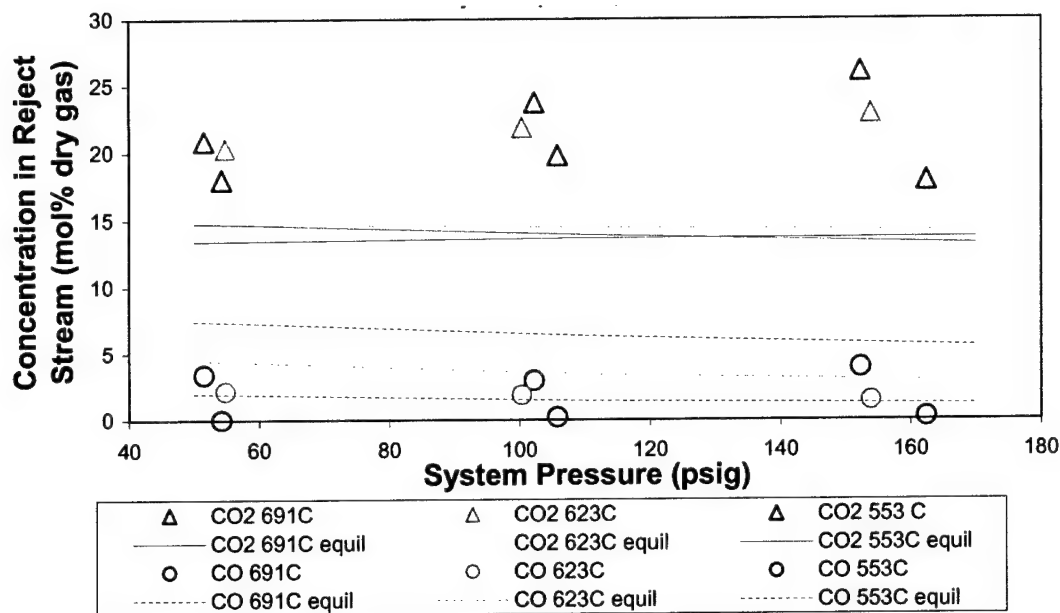
Figure 7: JP-8 Breadboard Reformer System -- Concentration of waste components in reject stream at steady state conditions with S/C = 5

The breadboard effort provided a wealth of information and lessons that helped in the design and execution of the 3kW lab demo unit. During test runs, it became clear that the steam reformer design with embedded hydrogen membrane would not permeate enough hydrogen to match its targeted design flow rate. Because of operating pressures and temperatures, a thick palladium membrane was required resulting in poor permeability. The application of hydrogen membrane is best suited for a downstream unit separate from the steam reformer. This approach will allow the unit to operate at lower temperatures with better mechanical support, which can result in using thinner membrane improving its permeability. Recently marketed palladium membrane unit by IdaTech, of Oregon, is a good example of this application. Due to the high cost of palladium membranes, research efforts are needed to develop a suitable and cost effective hydrogen purification technology.

One major problem in reforming JP8 is coking. Neither the Sud-Chemie reforming catalyst nor the cracking catalyst accumulated coke during operations. During breadboard runs un-catalyzed Pyrolysis of JP-8 and/or cracking residual material in stainless tubes at temperatures >400C occurred. The solution may be to minimize residence time in these hot zones or keep operating temperature under 400C. The solution used proved successful, a special alloy tube and high flow rate at coking location. A low temperature cracking process will eliminate coking potential.
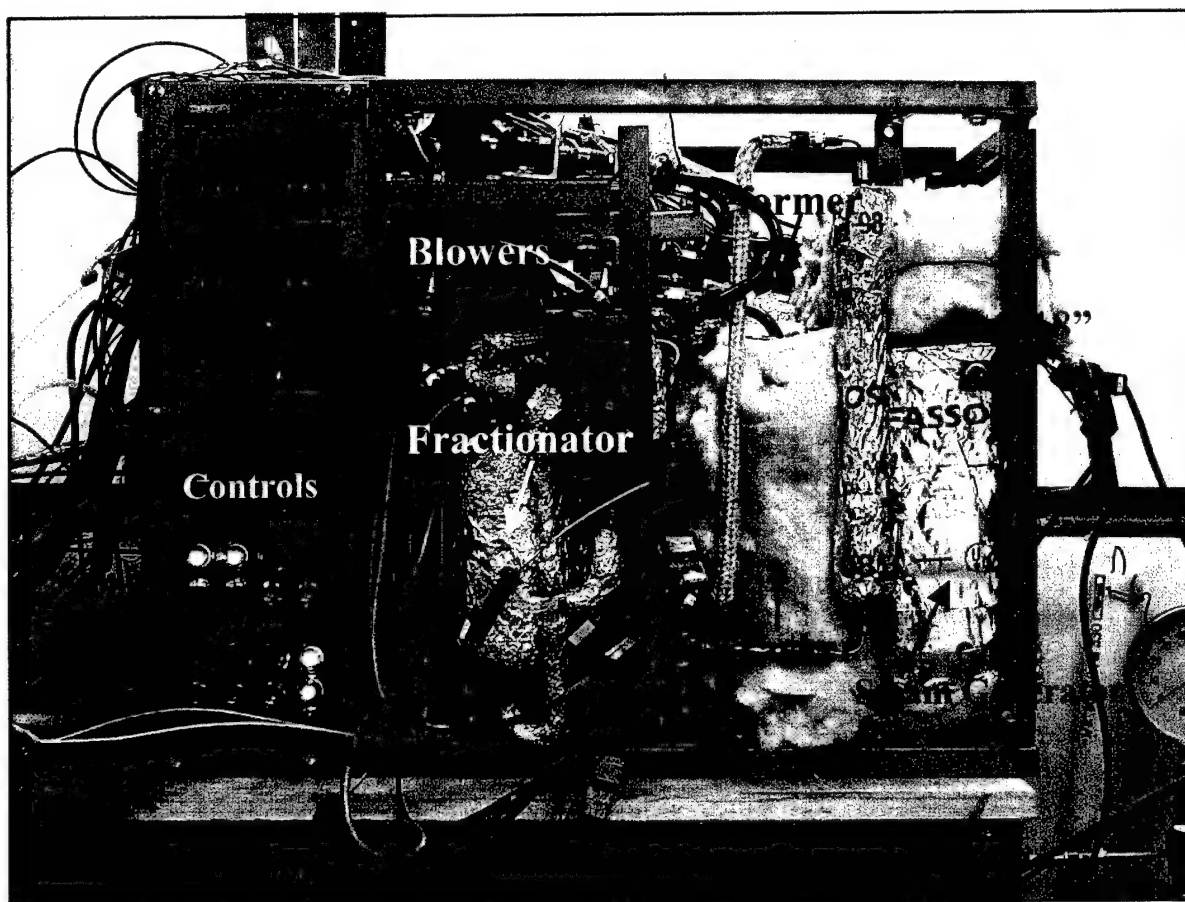
5.   3 KW LOGISTIC FUEL PROCESSOR LAB-DEMO

Based on lessons learned from the breadboard effort, a 3kW fuel processor has been designed and fabricated using packed bed reactors and JP-8 burners, Figure 8. The unit includes electronic controllers, air blowers, and fuel injectors along with pressure, flow, and temperature

sensors. With no hydrogen membrane or CO removal steps, the lab-demo is suitable for use with a 3kW Solid Oxide Fuel Cell (SOFC) stack.

5.1   3 kW Design and Development

The 3kW fuel processor has two process streams that mix. These are fuel and steam. In the first process stream, JP-8 partially evaporates as it passes through a series of recuperating heat exchangers. After the heat exchangers, the fuel enters the fractionator. From the fractionator, more than two-third of the fuel by weight leaves as vapor, and the remaining heavy fractions discharge to a fuel reservoir. The heavy liquid feeds the three burners that heat the cracker, steam generator, and steam reformer. The lighter, vaporized two-thirds passes into the cracker, where pelletized cracking catalyst breaks down the higher molecular weight hydrocarbons into lighter molecules, primarily ethylene, methane, and propylene.

Figure 8: 3 kW Logistic Fuel Processor Lab-Demonstration Unit

The cracker is a cylinder with 3" outer diameter and 1.5" inner diameter. The annular block, houses 9 cylindrical reactors evenly distributed, surrounds a cylindrical burner. The burner is made of woven metal. A fuel injector delivers the heavy fraction of JP-8, and a DC-driven blower provides air for the burner. Immediately after the cracker, the vaporized fuel enters the first zinc-oxide bed for sulfur absorption. A recuperating heat exchanger cools the fluid, which then passes through a liquid-vapor separator and then the second zinc-oxide bed. The fractionated, cracked, and desulfurized light fraction of fuel is now ready to mix with the second process stream, the superheated steam.

The two streams, cracked fuel and superheated steam, mix before entering the steam reformer. The steam reformer has a similar design as the cracker. Once the product stream leaves the steam reformer, it is ready to feed into a solid oxide fuel cell. In the laboratory operation, the product stream passes through a water-cooled heat exchanger, a backpressure valve, and a water-gas separator. These components reduce the temperature and remove water prior to the flow meter. The cool stream is also sampled for gas chromatography. The backpressure valve can provide a mechanical load equivalent to a fuel cell. It has been set to one atm absolute (fully open).

5.2 3 kW Results

The 3kW Reformer system was operated with a 4:1 steam to carbon ratio. Reactions were governed by equilibrium conditions. Data from experimental sets are provided in Table 2 and
Figure 9.

The fuel processor generated reformate stream sufficient to feed a 3 kW fuel cell. A SOFC with 60% conversion efficiency was assumed to calculate for all data fuel cell output. During the later data sets, more than 66 wt% of JP-8 passed to the cracker. Typical operation starts around 7:30 am and stops at 3:30 pm. After approximately 250 hours of hydrogen production, residual sulfur remained below the detection limit of 0.4 ppmv. Data was typically acquired during periods of 15 minutes to 2 hours of moderately steady operation.

Table 2: Product stream composition and flow rate from the 3kW Reformer Lab-Demo

	H2	CO	CH4	CO2	C2H4	C2H6	C3H6	Total	Product Flow Rate	Total Power (LHV)	SOFC Power
	[mol%]	[mol%]	[mol%]	[mol%]	[mol%]	[mol%]	[mol%]	[mol%]	[SLPM]	[kW]	[kW]
1	66%	0.6%	8%	21%	1%	3%	0.6%	100%	6	1.2	0.7
2	59%	6%	11%	17%	3%	2%	1%	100%	23	5.1	3.0
3	70%	2%	1%	27%				100%	40	4.9	3.0
4	75%	3%	4%	18%				100%	37	5.6	3.4

The first data set, in Table 2, is an average of 21 samples from five initial experiments. The others come from individual experiments. The second set is an average of two samples. The third is a single sample. The CO_2 in the third set is unrealistically high possibly due to the inclusion of water vapor, making the other components and SOFC power appear low. The fourth is an average of four samples. System modifications were made between each set. The data sets are numbered chronologically.
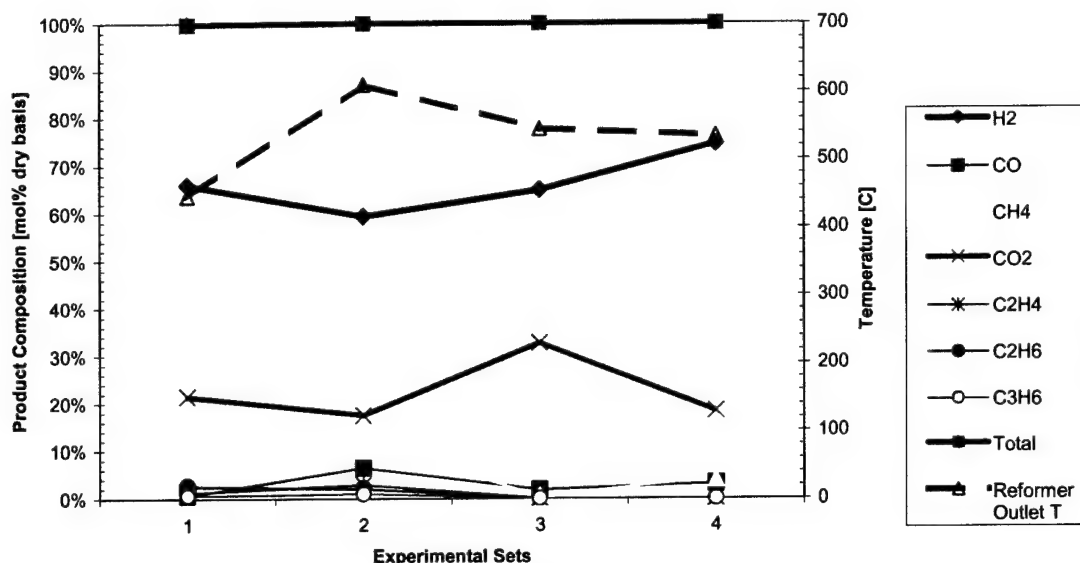

Figure 9: Product stream from the 3kw Reformer Lab-Demo; Data is taken from adjoining table.

In addition to achieving the capacity goal, the 3 kW Reformer lab-demo effectively removed sulfur. The 490ppm total sulfur typically found in JP-8 [4] has been reduced to undetectable levels. Sulfur content in the product stream was measured using Gas Chromatography with Pulsed Flame Photometric Detection (GC-PFPD). The GC-PFPD method had a single-species detection limit of 0.4 ppmv, and was capable of detecting all sulfur species that were likely to appear in the product stream, including hydrogen sulfide, methane- and ethane-thiols, thiophenes, and benzothiophenes. None of these species was detected. Figure 10 shows GC-PFPD chromatograms (sulfur signal) from analyses of the JP-8 fuel feed, the reformate stream, and a 20 ppmv SO_2/N_2 standard. Most of the sulfur in the JP-8 feed in Figure 10(a) is present as benzothiophenes, which elute between 17 and 27 minutes in the GC-PFPD method. No sulfur peaks above the method detection limit were observed in the reformate stream in Figure 10(b). (Two small peaks eluting after 30 minutes in Figure 10(b) were GC system contaminants). The scale of a 20 ppmv peak is shown in Figure 10(c) for comparison. Figure 10(b) and Figure 10(c) data were from 15 µL injection volumes of gases, while Figure 10(a) data was from a 0.2 µL injection of liquid. Otherwise, all analytical parameters were identical. The GC-PFPD result of "undetectable" for sulfur content in the reformate stream was qualitatively verified using a hydrogen sulfide – specific Dräger tube. The Dräger tube showed no color change after several minutes of exposure to the product stream.
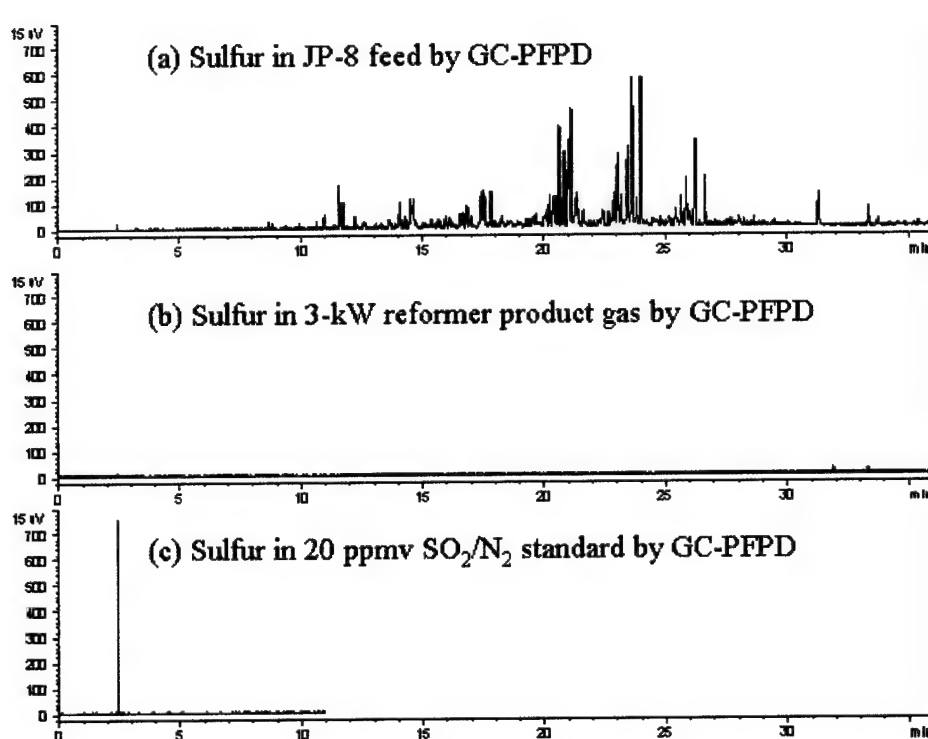
Figure 10: GC-PFPD (sulfur signal) chromatograms of (a) JP-8 fuel feed, (b) reformer product gas, and (c) a 20 ppmv SO_2/N_2 gas standard.

6. CONCLUSION

1. Processing heavy hydrocarbons; such as the military logistic fuel, diesel, and kerosene; to produce hydrogen stream suitable for fuel cell use has made possible with the use of a pretreatment step to remove sulfur and non-volatiles from the fuel. The pretreatment step consists of fractionation, light and heavy fractions separation, catalytic cracking, high temperature sulfur scrubbing, liquid-gas separation, and low temperature polishing. The pretreatment step delivers to the steam reformer a clean light gas fuel with sulfur content below the detection limit of 0.4ppmv. The fractionation of the fuel into lights and heavies streams, has allowed the process to reform the light fractions of the fuel that contain only 15% of the sulfur content, resulting in the maximum size reduction of sulfur scrubber beds.

2. Poor permeability plagues current hydrogen membrane technology. Although the REB reactor was designed for 3kW unit, it is unlikely that design will ever be practical for >2 kW reformer systems without significantly improved membrane performance. More research efforts are needed to develop a suitable hydrogen purification technology.

3. Neither the Sud-Chemie reforming catalyst nor the cracking catalyst accumulated coke during high-pressure operations. During breadboard runs un-catalyzed Pyrolysis of JP-8

and/or cracking residual material in stainless tubes at temperatures >400C occurred. The solution may be to minimize residence time in these hot zones or keep operating temperature under 400C. The solution may be to minimize residence time in these hot zones or keep operating temperature under 400C. The solution used proved successful, a special alloy tube and high flow rate at coking location. A low temperature cracking process will eliminate coking potential.

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APPENDIX I

DESCRIPTION OF THE FUEL PROCESSOR
COMPONENTS AND FLOW STREAMS

Stream labels:

1. Heated fuel feed
2. Vapor from partial evaporator
3. Light hydrocarbon gas, H_2, and H_2S from pre-reactor
4. Partially desulfurized light hydrocarbon
5. Sulfur reject
6. Desulfurized light hydrocarbon gas to reformer
7. Reject gas stream from reformer
8. Steam to reformer
9. Uncracked residual liquid from pre-reactor
10. Bottoms liquid from partial evaporator
11. Fuel to water evaporator burner
12. Fuel to steam reformer burner
13. Fuel to Desulfurizer burner
14. Fuel to cracking burner
15. Fuel to partial evaporator burner

Component descriptions

Partial evaporator – Continuous fractionation column that separates the fuel feed into vapor and bottom liquid fractions. Sulfur in middle distillate fuels such as diesel, Jet-A, JP-8, and kerosene is distributed predominantly in the higher end of the fuel's boiling range. These fuels can also contain nonvolatile hydrocarbons such as asphaltenes, and organo-metal compounds. The bottoms stream from the partial evaporator is enriched in sulfur, organic nonvolatiles, and metals relative to the feed, while the vapor stream is enriched in lower-boiling hydrocarbons and is depleted of contaminants that could poison or deactivate downstream components. The ratio of vapor to bottom liquid depends on the temperature and the system operating pressure, while the separation efficiency depends on the evaporator design.

Cracking Reactor – Packed bed catalytic reactor that catalytically cracks vapor hydrocarbons to hydrogen and light hydrocarbons. The catalyst used in the cracking reactor is selected to have the following properties: 1) High selectivity to light hydrocarbons and low selectivity to coke; 2) Good H-transfer activity so that organo-sulfur compounds are cracked to H_2S and light hydrocarbons at a high conversion rate; 3) Good catalytic cracking activity for aliphatic and aromatic hydrocarbons at the specified temperature. The ratio of light hydrocarbon gas to uncracked residual liquid obtained depends on the temperature, the system operating pressure, the cracking reactor space velocity, and the activity of the catalyst.

Desulfurizer – Flow-through gas-solid or gas-liquid process which removes H_2S from the light hydrocarbon stream prior to reforming. May use adsorbents such as ZnO or commercial preparations thereof, or other commercially available H_2S adsorbents, or a continuously regenerable solid- or liquid-phase H_2S adsorbent or absorbent.

Water Evaporator – A heat exchanger designed for efficient vaporization and superheating of feed H_2O.

Steam Reformer – Catalytic membrane reactor designed to produce H_2, CO, and CO_2 from light hydrocarbons and steam at a high conversion rate, while selectively separating the H_2 product from the byproducts. Reject stream from the reformer can contain H_2, CO, CO_2, and unreacted H_2O and hydrocarbons. All or a portion of the reject stream can be combusted in the burner.

Burner – System in which partial evaporator bottoms, uncracked pre-reactor residual liquid, and reject gas from reformer are mixed with air and combusted to provide heat for evaporator, pre-reactor, steam generator, and reformer operations. System may include one or more combustors designed for efficient heat transfer to components. The overall efficiency of the fuel processor system is maximized when the temperatures of the system are controlled so that the quantities of evaporator bottoms, uncracked residual liquid, and reject gas from reformer are exactly sufficient to supply the heat requirements of all endothermic operations and heat losses.